*Macromol. Symp.* **2003**, *197*, 171—180

# Mechanical and Thermal Properties of Rigid Polyurethane Foams Derived from Sodium Lignosulfonate Mixed with Diethylene-, Triethylene- and Polyethylene Glycols

*T. Hatakeyama,*[1] Y. Asano,[2] H. Hatakeyama[2]*

[1]Otsuma Women's University, 12, Sanban-cho, Chiyoda-ku, Tokyo 102-8357, Japan
[2]Fukui University of Technology, 3-6-1 Gakuen, Fukui 910-8505, Japan

**Summary:** Sodium salt of lignosulfonic acid (LS), which was obtained as by-product of cooking process in sulfite pulping, was solved in diethylene, triethylene or polyethylene glycol. Three series of polyurethane foams (LSPU) were synthesized by varying the LS content from 0 to 33 wt %. Apparent density ($\rho$) of LSPU foams ranged from 0.08 to 0.18 g cm$^{-3}$ and was affected by both LS content and oxyethylene chain length. Glass transition temperatures increased with increasing amount of LS and with decreasing oxyethylene chain length. Thermal gravimetry analysis indicated that the LS component decomposes first and that the thermal stability increases with decreasing oxyethylene chain length. Compression strength and compression modulus increased linearly with increasing apparent density. It is concluded that LS is successfully utilized as a hard segment of rigid PU foams, whose thermal and mechanical properties can be tuned by changing the amount of LS and the length of soft oxyethylene chains.

**Keywords:** compression strength; glass transition; lignosulfonate; poly(ethylene glycol); polyurethane

## Introduction

Lignosulfonic acid (LS) is ordinarily obtained in the sodium salt form as by-product of the cooking process in sulfite pulping.[1,2] In the solid state, LS is amorphous and its molecular motion is markedly restricted by ionic inter-molecular linkages.[3] X-ray diffractogram of LS shows a diffused pattern indicating a broad size distribution of molecular chains.[4] However, glass transition is not clearly observed by differential scanning calorimetry (DSC) due to the restriction of free molecular movement.[3]

LS is a polyelectrolyte and in aqueous solution shows amphiphilic properties since LS consists of C6-C3 hydrophobic basic structure with hydrophilic groups such as sulfonic, hydroxyl and

© 2003 WILEY-VCH Verlag GmbH & KGaA, Weinheim DOI: 10.1002/masy.200350716

carboxyl groups. Although LS has been used as dispersant in civil construction and other industrial applications, a large amount of LS is not effectively utilized.

We have paid special attention to the utilization of lignin which is a halfly made raw material for the synthesis of useful plastics and composites.[5-12] In our previous studies, polyurethanes (PU) in both sheet and foam shapes were derived from Kraft lignin and solvolysis (alcoholysis) lignin.[5-12] In the above synthesis, hydroxyl groups in lignin were used as reaction sites. By controlling the experimental conditions, mechanical and thermal properties could be varied in a wide range. The amount of lignin in PU is crucial in order to control the physical properties, since lignin molecules act as hard segments in the polyurethane chains.

In this study, we paid attention to utilization of LS. Although LS is water soluble, it is known that LS is insoluble in common organic solvents. This is the reason why LS has not been used as a reaction component. However, it is known that LS can be soluble in certain kinds of organic solvents, such as poly(ethylene glycol). We developed novel polyurethane rigid foams (LSPU) using the above special characteristics of LS.[12] Mechanical and thermal properties of LSPU are important when they are utilized in various industrial fields. In the present study, compression strength and thermal stability of LSPU are investigated.

## Experimental

### *Sample Preparation*

Sodium (Na) lignosulfonate (commercial name Vanilex HW) was provided by Nihon Seishi Co Ltd. According to the manufacture's report, the samples were purified after partial desulfonation; the content of sulfonate, carboxyl, alcoholic hydroxyl and phenolic hydroxyl groups was 0.13, 0.26, 0.28 and 0.42 moles per C6-C3 unit respectively. Three series of polyurethanes from LS (LSPU) were synthesized according to a previously reported procedure.[12] Diethylene glycol (DEG), triethylene glycol (TEG) and poly(ethylene glycol) with molecular mass of 200 (PEG200) were used as flexible component of PU. The above three oligo(ethylene glycol)s were provided by from Kanoto Chemical Industries, Ltd. According to the manufacturer's report, each sample is constituted by a mixture of oligomers. For example, TEG contains a traceable amount

© 2003 WILEY-VCH Verlag GmbH & KGaA, Weinheim

of DEG and tetraethylene glycol. LS was dissolved in DEG, TEG or PEG at a temperature included between 65 and 75 °C. The LS content of the above solution was varied from 0 to 33 %. The LS content of the system was calculated as follows.

$$\text{LS content (\%)} = 100m_{\mathrm{LS}} / (m_{\mathrm{LS}} + m_{\mathrm{DEG,\ TEG\ or\ PEG}}) \qquad (1)$$

where $m_{\mathrm{LS}}$ is mass of LS and $m_{\mathrm{DEG,\ TEG\ or\ PEG}}$ is mass of DEG, TEG or PEG. The above polyol solution was mixed with a small amount of surfactant (silicone surfactant), catalyst (di-*n*-butyltin dilaurate) and foaming agent (water). This premixture was reacted with diphenylmethane diisocyanate (MDI) under vigorous stirring at room temperature. NCO/OH ratio was 1.2. After foams were obtained, the samples were allowed to stand overnight at room temperature. PU's containing the above three different kinds of oligo(ethylene glycol) are designated as LSDPU, LSTPU and LSPPU, respectively. A schematic representation of the sample chemical structure is shown in Figure 1.

### *Apparent Density*

Apparent density ($\rho$, g cm$^{-3}$) was calculated from mass and volume. Size of sample was 4.0 x 4.0 x 3.0 cm.

### *Stress-strain Measurement*

A Shimadzu Autograph AG-2000D was used for uni-axial compression strength tests. The sample was rectangular shape whose cross section was 4.0 x 4.0 cm and the length was 3.0 cm. Compression rate was 0.3 cm min$^{-1}$. Compression strength ($\sigma_{10}$, Pa) was calculated at 10 % strain. The yielding strength ($\sigma_y$) was evaluated as the maximum strength from stress-strain curve. The compression modulus was calculated from the initial tangent of stress-strain curve.

### *Thermogravimetry*

Thermogravimetry (TG) was carried out in nitrogen (flow rate = 200 ml min$^{-1}$) using a Seiko TG 220 instrument at a heating rate of 20 °C min$^{-1}$ in the temperature range from 20 to 800 °C. Sample mass was ca. 5 mg.

© 2003 WILEY-VCH Verlag GmbH & KGaA, Weinheim

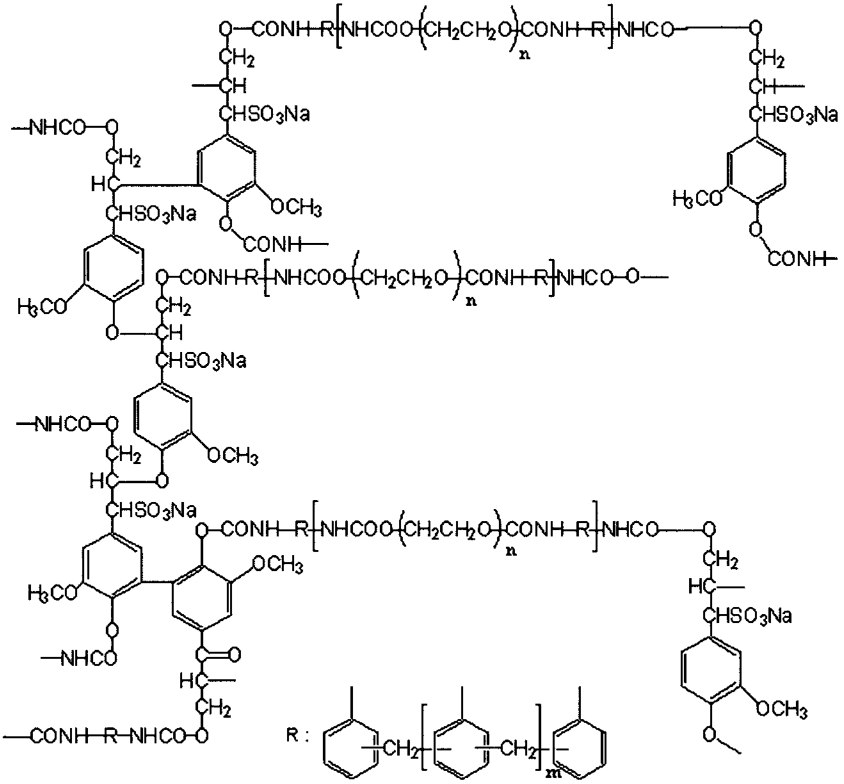

Figure 1. Schematic representation of the chemical structure of LSPU

*Differential Scanning Calorimetry*

Differential scanning calorimetry (DSC) was performed using a Seiko DSC 220 instrument at a heating rate of 10 °C min$^{-1}$ under a nitrogen flow (flow rate = 30 ml min$^{-1}$). Sample mass was 5 ~ 10 mg. Aluminum open pans were used. The samples were heated to 200 °C and cooled at 40 °C min$^{-1}$ to -120 °C. DSC scans were repeated 2 times. The results of the second run were used for the determination of glass transition temperature ($T_g$) and heat capacity variation at $T_g$ ($\Delta C_p$).[13]

*Scanning Electron Microscopy*

Scanning electron microscopy (SEM) was carried out using a JEOL JSM-5510LV instrument at 1.0 kV accelerating voltage. The sample was broken and coated with Au.

© 2003 WILEY-VCH Verlag GmbH & KGaA, Weinheim

## Results and Discussion

The color of rigid polyurethane (PU) foams varied from brown to dark brown according to LS content. Figure 2 shows scanning electron micrographs of representative LSPU samples with 20% LS content. The poor diameter, which was measured by scanning electron microscopy varied from 100 to 300 x $10^{-3}$ cm. No large morphological difference was observed among LSDPU, LSTPU and LSPPU samples when the LS content was the same. When the LS content was larger than 30 %, LSPU was not homogeneously foamed. Therefore, mechanical data of the samples with LS content greater than 30 % were omitted from the results.

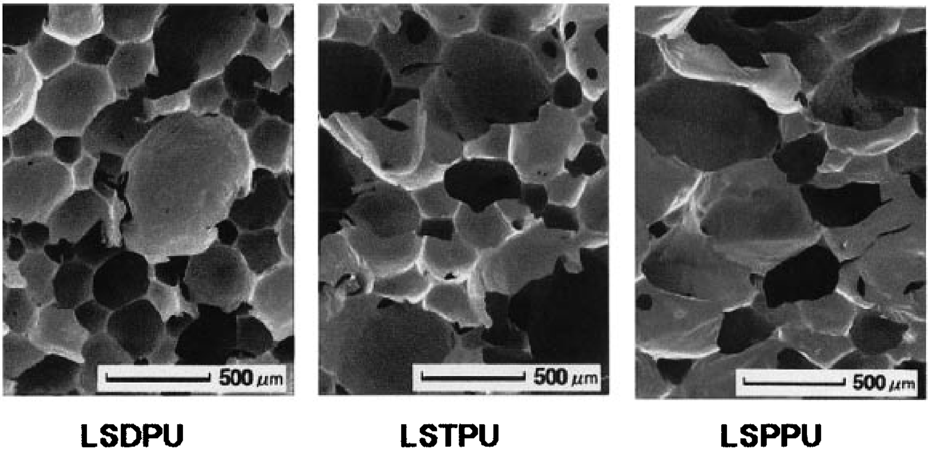

Figure 2. Scanning electron micrographs of LSDPU, LSTPU and LSPPU at 20% LC content.

Figure 3 shows apparent density ($\rho$) of LSPU samples presented three dimensionally. Symbol *n* in the figure indicates the number of *n*-mer of ethylene glycol. As stated in the experimental section, *n* is an average value. Values of $\rho$ range from 0.08 to 0.12 g $cm^{-3}$. As shown in Figure 3, the minimum $\rho$ values were observed at about 20% LS contents. The dependency of $\rho$ on LS contents increases with increasing *n*. As the diameter of the pores is almost the same for all PU samples, variation of $\rho$ is attributable to the wall thickness of pores. The fact that $\rho$ values

© 2003 WILEY-VCH Verlag GmbH & KGaA, Weinheim

increase with increasing *n* indicates that the foaming ability is markedly affected by molecular length of oxyethylene chains.

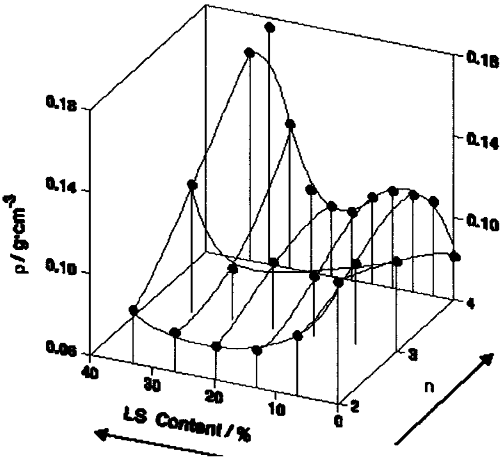

Figure 3. Dependence of the apparent density ($\rho$ / g cm$^{-3}$) on LS content (%) and number ($n$) of units ethylene glycol oligomers

When the samples were heated from -120 to 200 °C, a major variation of the heat capacity due to glass transition was observed between 80 and 140 °C. The glass transition temperature ($T_g$) was defined as schematically shown in the left side of Figure 4. It is reported that $T_g$ of LS is not clearly observed due to intermolecular ionic bondings.[3] In the case of LSDPU, $T_g$ was clearly identified. Heat capacity difference at $T_g$ ($\Delta C_p$) of LSPU ranged from 0.35 to 0.15 J g$^{-1}$ K$^{-1}$. The recorded $\Delta C_p$ values are smaller than those found in common synthetic amorphous polymers.[14] This suggests that molecular motion of LSPU is restricted by urethane linkage. As shown in Figure 4, the $T_g$ of LSPU samples increases with increasing LS content and decreasing *n* values. This indicates that long flexible oxyethylene chains enchance free molecular motions. LS content dependency is significant for LSPPU but scarcely observed for LSDPU.

© 2003 WILEY-VCH Verlag GmbH & KGaA, Weinheim

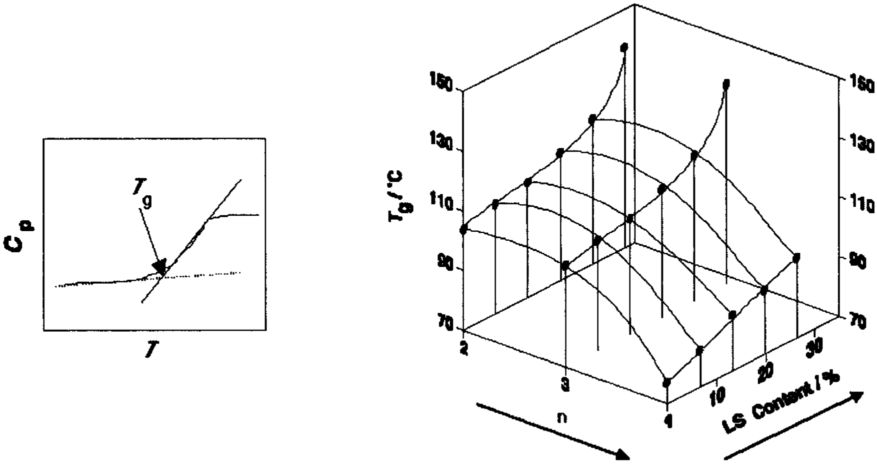

Figure 4. Schematic definition of $T_g$ (left) and dependence of the $T_g$ of polyurethane samples on LS content and *n*

The thermal decomposition of various type of lignin and its derivatives including PU was studied by many researchers[8,10,15,16,17] and the nature of gases evolved during decomposition was also reported.[10] LSPU starts to decompose at around 280 °C ($T_{di}$). The urethane linkage formed between phenolyc hydroxyl groups and isocyanate starts to dissociate at around 280 °C. The decomposition temperature ($T_d$) defined as shown in the schematic curve (left part of Figure 5) was included in the 290-300 °C range. The major mass decrease is attributable to the decomposition of LS. Furthermore, a second decomposition step was observed for all kinds of samples and was attributed to the decomposition of oxyethylene chains. In this study, peak temperature of TG derivatives was used as an index of decomposition temperature. Two peak temperatures were defined as $\Delta T_{d1}$ and $\Delta T_{d2}$ for the low temperature and for the high temperature peak. As shown in Figure 5, the length of oxyethylene chains markedly affects $\Delta T_{d2}$ values, however, no characteristic tendency was observed for $\Delta T_{d1}$. Both $\Delta T_{d1}$ and $\Delta T_{d2}$, decrease with increasing LS content, suggesting that the LS decomposition products further accelerate the LS decomposition.

© 2003 WILEY-VCH Verlag GmbH & KGaA, Weinheim

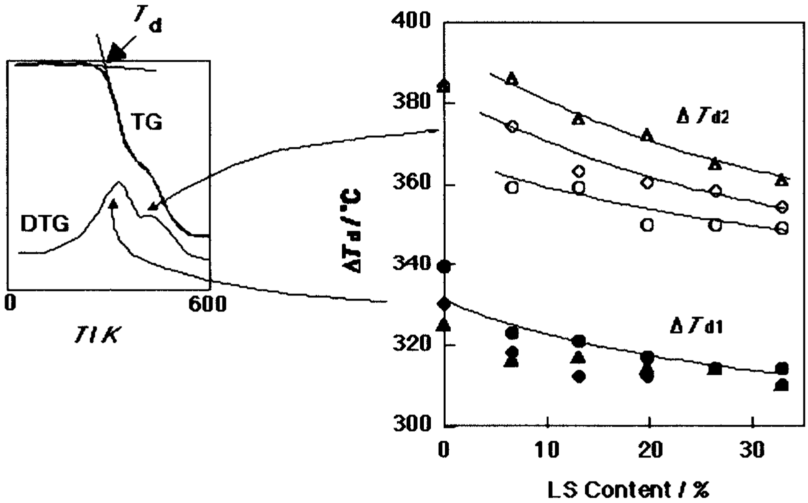

Figure 5. Schematic definition of $T_d$ (left) and dependence of $\Delta T_{d1}$ and $\Delta T_{d2}$ on LS content (right)

Figure 6 shows of the dependence of the amount of residue of 450°C on the LS content. Although values are scattered, the general tendency indicates that amount of mass residue increases with increasing LS content. At the same time, it is clearly seen that length of oxyethylene chains affects the mass residue. This also suggests that the major part of residual carbon is attributable to the LS component. The densely packed structure due to short flexible chains depresses diffusion of evolved gases.

Figure 7 shows compression strength ($\sigma_{10}$) at 10 % strain and yielding strength ($\sigma_y$) as a function of apparent density ($\rho$). All data are on a single straight line, showing that macrostructure of LSPU affects mainly mechanical properties. As shown in Figure 2, the size of pores is almost the same regardless of oxyethylene chain length, thickness of the wall is thought to be a major factor controlling the compression stress. As already presented in Figure 3, apparent densities of LSPPU are larger than those of LSTPU or LSDPU. When the results of Figure 7 are examined more precisely, compression stresses of LSDPU are found in the low apparent density range and those of LSPPU are observed in the high density range. These results suggest that the foaming

© 2003 WILEY-VCH Verlag GmbH & KGaA, Weinheim

process is also controlled by the flexibility of the soft segment. Therefore, the amount of LS content and number of oxyethylene chains affects mechanical properties through apparent densities. Figure 8 shows the relationship between compression modulus and apparent density. A linear dependence is observed, although data are scattered.

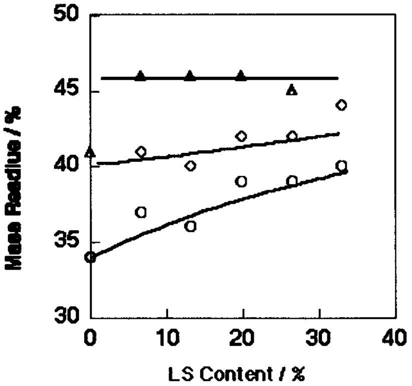

Figure 6. Mass residue at 450 °C as a function of LS content in LSPU. O = LSPPU, ◇ = LSTPU, △ = LSDPU

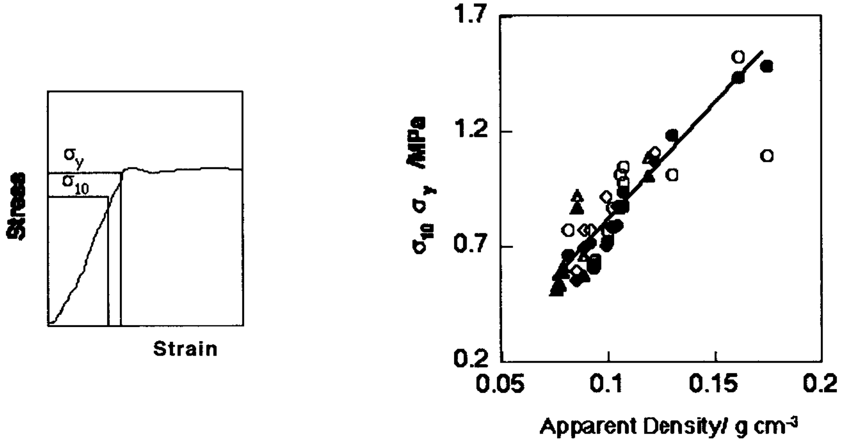

Figure 7. Dependence of the strength at 10 % strain ($\sigma_{10}$; ● = LSPPU, ◆ = LSTPU, ▲ = LSDPU) and of the strength at yielding point ($\sigma_y$; O = LSPPU, ◇ = LSTPU, △ = LSDPU) on the apparent density of polyurethanes

© 2003 WILEY-VCH Verlag GmbH & KGaA, Weinheim

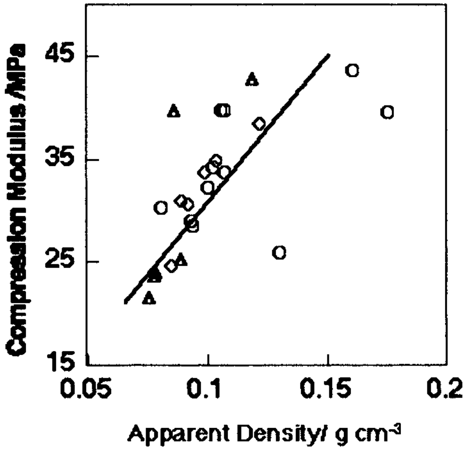

Figure 8. Relationship between compression modulus and apparent density. O = LSPPU, ◇ = LSTPU, △ = LSDPU

From the above results, it is concluded that LS is successfully utilized as a hard segment of rigid PU foams, whose thermal and mechanical properties are controllable by changing the amount of LS content and molecular length of the soft oxyethylene segments.

[1] W. G. Glasser, S. S. Kelly, in *"Encyclopedia of Polymer Science and Engineering"*, John Wiley & Sons, New York 1987, 8, p.795.

[2] D. A. I Goring in "*Lingins*" K. V. Sarkanen, C. H. Ludwig, Eds., Wiley-Interscience, New York 1971, p.697.

[3] H. Hakaeyama, K. Nakamura, T. Hatakeyama, *Trans. Pulp Paper Canada* **1980**, 81, 105.

[4] T. Hatakeyama, H. Hatakeyama, *Polymer* **1982**, 23, 475.

[5] K. Nakamura, R. Morck, K. P. Kringstad, H. Hatakeyama, in "*Wood Processing and Utilization*", J. F. Kennedy, G. O. Phillips, Ellis Forwood, Chichester, 1989, p.175.

[6] H. Yoshida, R. Morck, K. P. Kringstad, H. Hatakeyama, *Appl. Polym. Sci.* **1990**, 40, 1819.

[7] K. Nakamura, R. Morck, K. P. Kringstad, H. Hatakeyama, *Polym. Adv. Technol.* **1991**, 2, 41.

[8] K. Nakamura, T. Hatakeyama, H. Hatakeyama, *Polym. Adv. Technol.* **1992**, 3, 151.

[9] J. Nakano, Y. Izuta, T. Orita, H. Hatakeyama, K. Kobashigawa, S. Hirose, *Sen-i Gakkaishi* **1997**, 53, 416.

[10] S. Hirose, K. Kobashigawa, Y. Izuta, H. Hatakeyama, *Polym. Int.* **1998**, 47, 247.

[11] T. Hatakeyama, Y. Izuta, S. Hirose, H. Hatakeyama, *Polymer* **2002**, 43, 1177.

[12] Y. Asano, H. Hatakeyama, *Memoirs Fukui Univ. Technol.* **2002**, 32, 275.

[13] T. Hatakeyama, F. X. Quinn, in "*Thermal Analysis*", John Wiley & Sons, Chichester, 1994, p.107.

[14] T. Hatakeyama, H. Hatakeyama, *Thermochimica Acta* **1995**, 267, 249.

[15] G. E. Domberg, V. N. Sergeeva, A. I. Kalininsh, *Therm. Anal.* **1972**, 2, 327.

[16] G. E. Domberg, G. A. Rossinskaya, V. N. Sergeeva, *Therm. Anal.* **1974**, 3, 211.

[17] S. Hirose, H. Hatakeyama, *Mokuzai Gakkaishi* **1986**, 43, 1.

© 2003 WILEY-VCH Verlag GmbH & KGaA, Weinheim